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IMPROVEMENT OF MICROWAVE ABSORPTION CHARACTERISTICS BY COATING LAYER IN SUBSTITUTED U-TYPE FERRITES

The U-type ferrite is a kind of hexagonal ferrite, and it is known as a microwave absorber in the X-band. The magnetic and dielectric loss of the U-type ferrite change to the composition and coating layer, etc. In this study, the silicon oxide layer was coated on the substituted U-type ferrites to improve microwave absorption characteristics. The complex permittivity and complex permeability were measured using toroidal specimens that were press-molded and the measured frequency range was set from 2-18 GHz. The improvement of the microwave absorption rate was different according to the type of the substituted U-type ferrites. Only in the substituted U-type ferrites with nickel and zinc, an improvement in the microwave absorption rate due to enhancement of magnetic loss was confirmed. The highest microwave absorption was 99.9% at 9.6 GHz, which was S_$Z_{0.5}$U.

Keywords: hexagonal ferrite, U-type ferrite, silicon oxide layer, microwave absorption

1. Introduction

In recent years, with the development of wireless communication technology, exposure to various microwave signals is increasing rapidly. The electromagnetic interference from these microwave signals is a serious problem that causes digital malfunction. This problem is expected to get worse in the future. Microwave absorbers are considered one of the effective solutions to this problem [1-10].

The U-type ferrite is one of the microwave absorbers in the X-band frequency (8.2-12.5 GHz), because of the large magneto-crystalline anisotropy and high saturation magnetization [2]. The U-type ferrite belongs to the hexagonal ferrite. And the hexaferrite is classified depending on their crystal structure and composition [2]. The U-type ferrite formula is expressed as $Ba_4Me_2Fe_{36}O_{60}$, where Me is a divalent transition metal such as cobalt, manganese, nickel, copper, zinc, etc. The U-type ferrite has a complex crystal structure with a combination of two hexaferrites which are M- and Y-type ferrite [3]. These ferrites are stacked on the *c*-axis so that U-type ferrite has a long specific crystal structure. Due to this unique crystal structure, the U-type ferrite has a large magnetocrystalline anisotropy [6]. Also, since the large molecular weight includes a relatively large number of magnetic ions, the saturation magnetization is high [9].

There have been reports of improvement of microwave absorption characteristics for iron micro-flakes by silicon dioxide (SiO_2) coating [11]. The effects of the SiO_2 coating resulted in the change of magnetic loss and dielectric loss, which are the main factors in absorption characteristics. We had studied changes in the microwave absorption characteristics of substituted U-type ferrites. The microwave absorption of substituted U-type ferrites resulted in a combination of magnetic and dielectric losses [12-13]. In this study, attention was paid to the improvement of absorption characteristics of the substituted U-type ferrites by the coated silicon oxide layer.

2. Experimental

In this study, the U-type ferrites were substituted U-type ferrites by the sol-gel method. The substituted U-type ferrites were partially substituted with divalent cobalt ions in $Ba_4Co_2Fe_{36}O_{60}$. The substitution elements were copper, manganese, nickel, and zinc. The substitution ratio was designed to be 0.5 in all samples. The sample names were distinguished by the initials and substi-

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tution ratio of the substitution elements. For example, the $C_{0.5}U$ means that 0.5 mol of Co is replaced with Cu. Also, the sample which has a silicon oxide (SiO_x) layer was distinguished by attaching S_ before sample name.

The starting materials that barium nitrate, manganese nitrate tetrahydrate, iron nitrate nonahydrate, cobalt acetate tetrahydrate, copper acetate, manganese nitrate tetrahydrate, nickel acetate hydrate, and zinc acetate dihydrate were weighed and mixed in DI water according to the designed stoichiometric ratio. The citric acid and the ethylene glycol were then added to the mixture and adjusted to pH 6 using the ammonia solution. After that, the mixture was stirred at 85°C for 8 hours to form a sol. The sol formed was subjected to a gelation process, and then heat-treated at 1300°C for 3 hours to obtain ferrite powders. The heat treatment condition was set based on the previous study [12-13].

The SiO_x layer coated by the modified Stöber process [11]. The substituted U-type ferrite powders were dispersed ultrasonically in ethanol. And then ammonium hydroxide solution and of TEOS (tetraethyl orthosilicate) added to the mixture. After that, the mixture stirred at 300 rpm for 2 hours. After the reaction, the powders were washed with ethanol and dried in an oven at 60°C for 12 hours.

The SiO_x layer was confirmed by TEM (TALOS, F200X). And magnetic property changes were measured by the VSM (Quantum Design, Versa Lab VSM, ±10 kOe, room temperature). Specimens for measuring microwave absorption characteristics were prepared in a toroidal shape by mixing paraffin and ferrite powder. The weight ratio of paraffin and powder was 1: 5 and all specimen thicknesses were 3.0 mm. The measurement frequency range was 2-18 GHz.

The Vector Network Analyzer (Agilent, PNA-X N5245A) was used to measure the complex scattering parameters. The measured scattering parameters were calculated the complex permeability ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and the complex permittivity ($\mu_r = \mu' - j\mu''$) from the software in the Vector Network Analyzer (Agilent software module 85071E). Reflection loss (R. L.) was calculated from the ε_r and the μ_r using the Eq. (1) and (2), where Z_m and Z_0 are the sample impedance and free space impedance. In Eq. (2), which describes the factors that determine the reflection loss, f, c, and t represent the frequency, the speed of light, and the thickness of the sample, respectively. Changes in the absorption characteristics were compared with $\tan\delta_\varepsilon$ ($= \varepsilon'' / \varepsilon'$, dielectric loss) and $\tan\delta_\mu$ ($= \mu'' / \mu'$, magnetic loss).

$$R.L. = -20 \log_{10}\left[\left(Z_m - Z_0\right)/\left(Z_m + Z_0\right)\right](dB) \quad (1)$$

$$Z_m = Z_0\sqrt{\mu_r / \varepsilon_r}\,\tan h\left[-\left(j2\pi f / c\right)\sqrt{\mu_r \varepsilon_r}\,t\right] \quad (2)$$

3. Results and discussion

Fig. 1 shows the coated SiO_x layer that was observed by TEM. It is an image of S_$C_{0.5}U$ ($Ba_4Cu_{0.5}Co_{1.5}Fe_{36}O_{60}$) among substituted U-type ferrites. Fig. 1(a) shows the TEM image in bright field mode, and Fig. 1(b) shows the EDS result. In Fig. 1(a), the coated layer thickness was observed to ~100 nm. Also, in the diffraction mode image of the SiO_x layer, concentric circles appearing in the amorphous material were shown. In Fig. 1(b), it was confirmed that the silicon atoms represented by the red dots were concentrated on the surface of the ferrite powder. And in the region corresponding to the ferrite powder shown in gray in Fig. 1(a), it was confirmed that the constituent elements of the ferrite powder, Ba, Co, Cu, and Fe were evenly distributed. Besides, yellow dots corresponding to the oxygen atoms included in the ferrite powder and the coated layer were found on both sides. The SiO_x layer formed through this was confirmed.

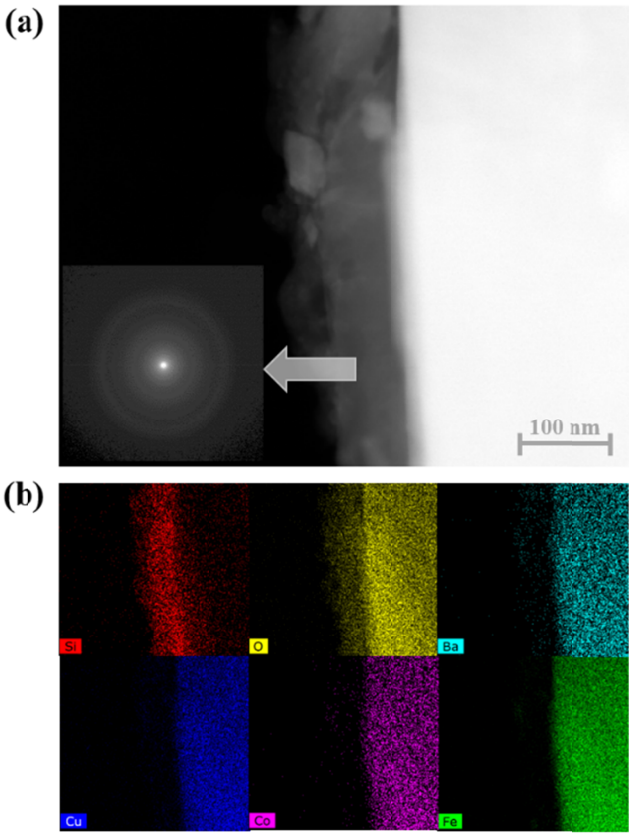

Fig. 1. (a) TEM image and (b) EDS mapping of S_$C_{0.5}U$ ($Ba_4Cu_{0.5}Co_{1.5}Fe_{36}O_{60}$)

The VSM results of ferrite powders measured before and after coating are shown in Fig. 2 and Table 1. In Fig. 2, the solid line and the dotted line represent before and after coating, respectively. As shown in Fig. 2, the soft magnetic properties were maintained after coating in all substituted U-type ferrites. Instead, the saturation magnetization of the coated samples in the same composition was decreased. This decrease was due to the influence of the SiO_x layer. Since the saturation magnetization was expressed by dividing the measured magnetization by the weight of the sample, the saturation magnetization was decreased in the coated samples containing the nonmagnetic SiO_x layer. The coercivities were slightly increased or decreased depending on the sample, but this was negligible in U-type ferrite with soft magnetic properties.

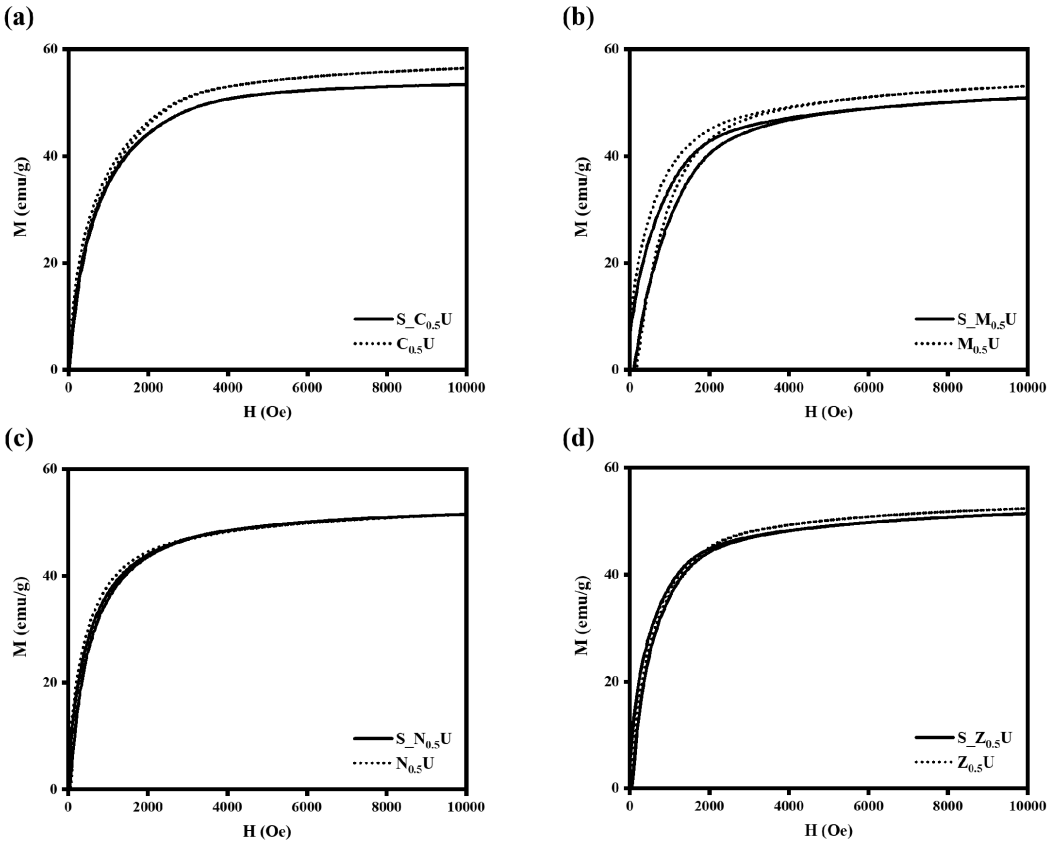

Fig. 2. *M-H* curves of SiO_x coated U-type ferrites; (a) S_$C_{0.5}$U, (b) S_$M_{0.5}$U, (c) S_$N_{0.5}$U, and (d) S_$Z_{0.5}$U

TABLE 1

Magnetic properties of U-type ferrites before and after SiO_x coating

Sample name	Saturation Magnetization (M_s, emu/g)	Coercivity (H_c, Oe)	Sample name	Saturation Magnetization (M_s, emu/g)	Coercivity (H_c, Oe)
$C_{0.5}U$	56.5	13.2	S_$C_{0.5}U$	53.0	16.3
$M_{0.5}U$	50.9	173.3	S_$M_{0.5}U$	48.7	109.4
$N_{0.5}U$	51.5	47.0	S_$N_{0.5}U$	51.5	51.4
$Z_{0.5}U$	51.6	46.9	S_$Z_{0.5}U$	51.4	48.0

Fig. 3 shows magnetic loss and dielectric loss converted to complex permeability and complex permittivity measured in toroidal samples. And Fig. 4 shows the reflection loss calculated from the complex permeability and the complex permittivity by Eq. (1) and (2). In both figures, the sample before the coating was represented by a dotted line, and the sample after coating was represented by a solid line.

Fig. 3(a) shows the comparison of magnetic loss ($\tan\delta_\mu$) and the dielectric loss ($\tan\delta_\varepsilon$) before and after coating in U-type ferrite partially substituted with Cu. In the $\tan\delta_\mu$ and $\tan\delta_\varepsilon$ of the sample before coating, there were peaks due to magnetic resonance at 16.8 GHz and 16.5 GHz, respectively. This means that the electromagnetic absorption in $C_{0.5}U$ was a combination of magnetic and dielectric losses. On the contrary, it was confirmed that the peaks disappear in $\tan\delta_\mu$ and $\tan\delta_\varepsilon$ of the coated sample. There was an effect of removing the high magnetic loss and the dielectric loss that occurred at a specific frequency by the SiO_x layer, and accordingly, as shown in Fig. 4(a), the microwave absorption rate decreased.

In Fig. 3(b), it was compared to $\tan\delta_\mu$ and $\tan\delta_\varepsilon$ in $M_{0.5}U$ that was partially substituted by Mn. The $\tan\delta_\mu$ and $\tan\delta_\varepsilon$ of the sample with the SiO_x layer represented by the solid line were below the dotted line in the entire measured frequency range. It means that both losses were reduced according to the formation of the coated layer, resulting in a decrease in the microwave absorption rate as shown in Fig. 4(b).

Fig. 3(c) and (d) show the changes $\tan\delta_\mu$ and $\tan\delta_\varepsilon$ according to the coating of the U-type ferrites with Ni and Zn partially substituted, respectively. They were different from S_$C_{0.5}$U and S_$M_{0.5}$U. Both samples were decreased $\tan\delta_\varepsilon$, however, $\tan\delta_\mu$ was rather increased. It was confirmed that the insulating layer, the SiO_x layer, attenuates the dielectric loss while strengthening the magnetic loss in $N_{0.5}U$ and $Z_{0.5}U$. As a result, as shown in Fig. 4(c) and (d), the microwave absorption rate was improved.

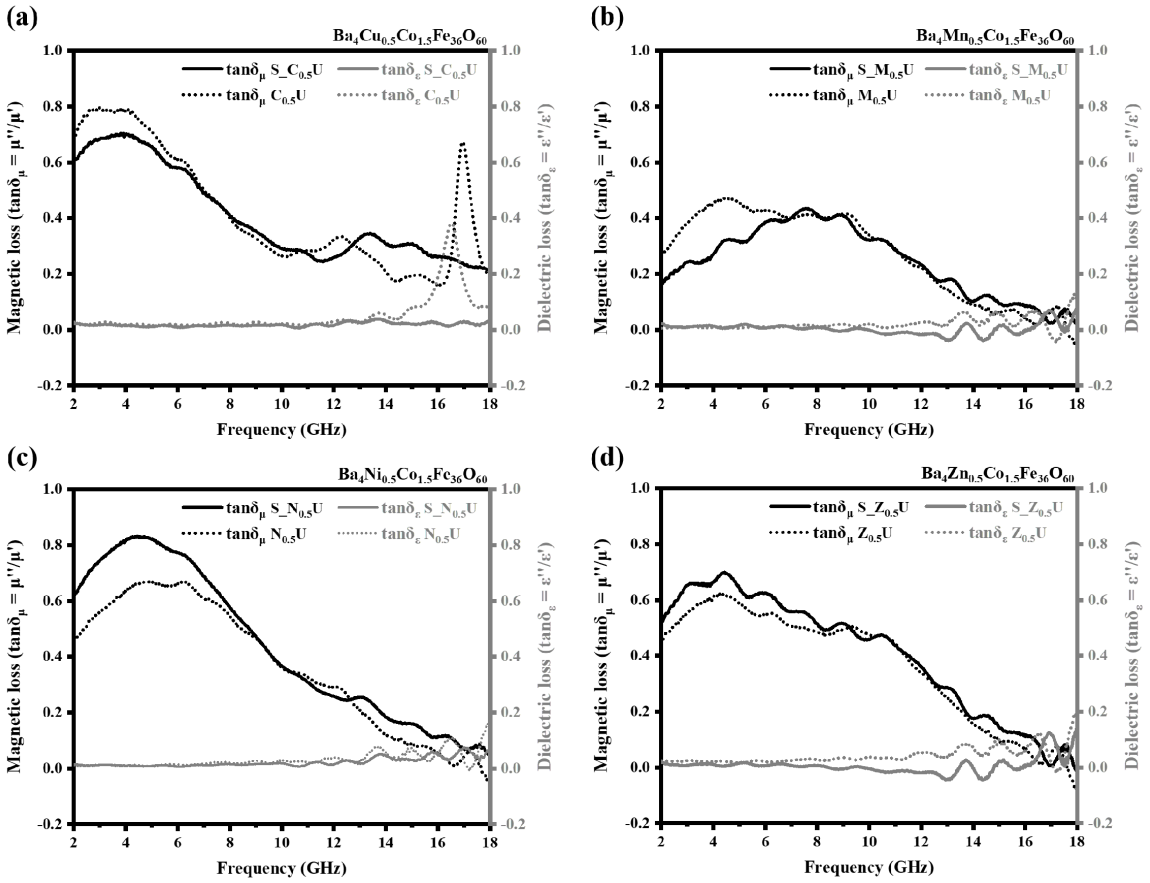

Fig. 3. Magnetic loss and dielectric loss of SiO_x coated U-type ferrites; (a) S_$C_{0.5}$U, (b) S_$M_{0.5}$U, (c) S_$N_{0.5}$U, and (d) S_$Z_{0.5}$U

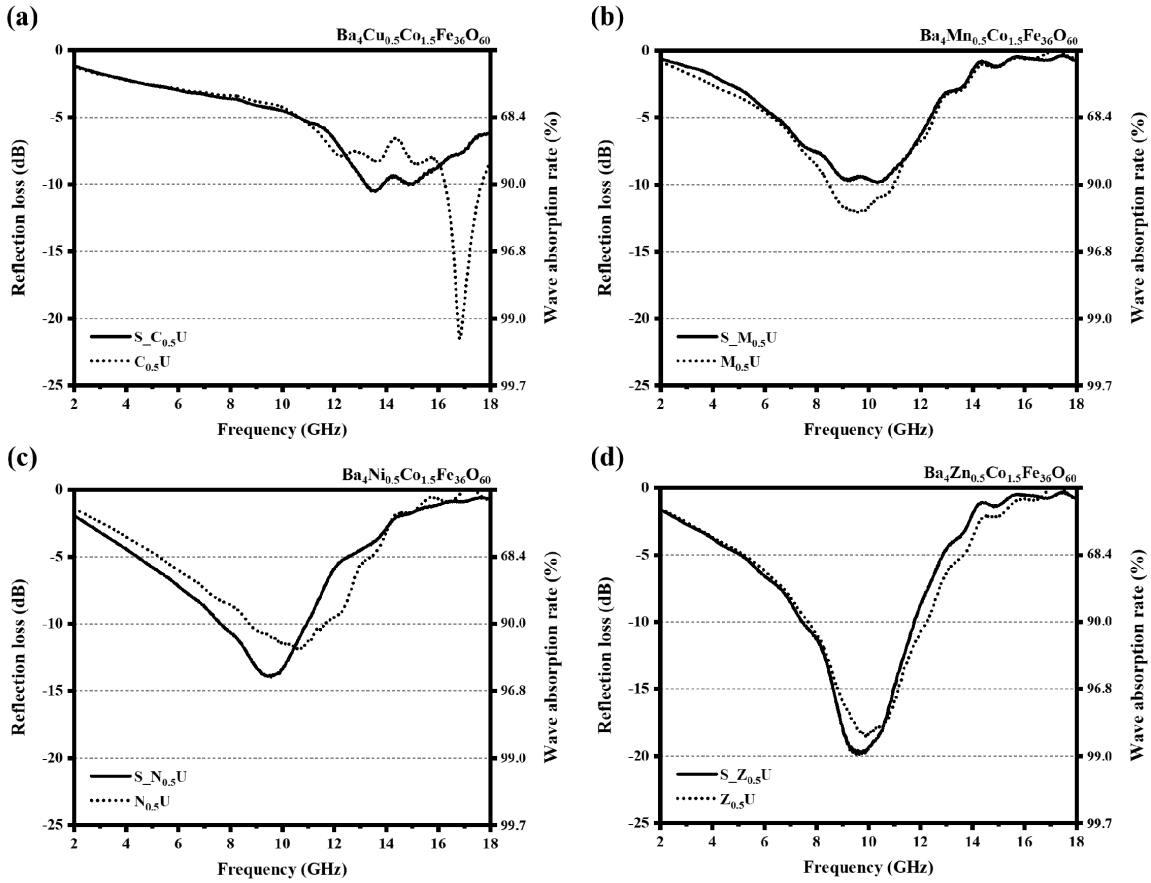

Fig. 4. Reflection loss of SiO_x coated U-type ferrites; (a) S_$C_{0.5}$U, (b) S_$M_{0.5}$U, (c) S_$N_{0.5}$U, and (d) S_$Z_{0.5}$U

Fig. 4 shows the change in the microwave absorption characteristics with the SiO_x layer. In the reflection loss of Fig. 4(a), $C_{0.5}U$ had a peak of -21.5 dB at 16.8 GHz. It translates to 99.3% when converted to the wave absorption rate. However, S_$C_{0.5}U$ was disappeared peak which caused in the combination of magnetic loss and genetic loss. It was because magnetic loss and dielectric loss were attenuated by SiO_x layer formation as mentioned in Fig. 3(a). This attenuation was the same in S_$M_{0.5}U$ shown in Fig. 4(b). Unlike S_$C_{0.5}U$ and S_$M_{0.5}U$, the wave absorption rate was improved in S_$N_{0.5}U$ and S_$Z_{0.5}U$ in Fig. 4(c) and (d). In Fig. 4(c), S_$N_{0.5}U$ shows that the microwave absorption rate was 93.5% (–11.9 dB) at 10.4 GHz before coating, and it was increased to 96.0% (–14.0 dB) at 9.5 GHz after coating. Also, S_$Z_{0.5}U$ had improved the wave absorption rate. In Fig. 4(d), the wave absorption rate was 98.6% (–18.5 dB) at 9.8 GHz in $Z_{0.5}U$, and 99.0% (–19.9 dB) at 9.6 GHz in S_$Z_{0.5}U$. The improvement of the absorption rate of both was attributed to the improvement of the magnetic loss.

4. Conclusions

In this study, the SiO_x layer was formed on the substituted U-type ferrite to improve the microwave absorption characteristics. It was confirmed that the thickness of the coating layer was ~100 nm, and the saturation magnetization was decreased according to the coating layer formation. The SiO_x layer was improved the microwave absorption rate in S_$N_{0.5}U$ and S_$Z_{0.5}U$. The cause of the improvement of the microwave absorption rate was due to the enhanced magnetic loss.

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